

Synthesis and photophysical properties of a novel benzanthrone pH sensor based on internal charge transfer

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A novel fluorescence sensing derivative of 3-aminobenzanthrone configured as a “fluorophore-receptor” system was synthesized by nucleophilic substitution of 3-aminobenzanthrone with benzoyl chloride. Synthesized compound was isolated, characterized and identified by TLC, UV-vis, IR and ¹H NMR spectra. Due to the internal charge transfer, the designed fluorophore was able to act as a pH-probe via an “off-on” fluorescence sensing mechanism. The sensor activity toward protons as cations and hydroxide as anions in solution of DMF/water (1:1) and on cellulose paper was studied by monitoring the changes of the fluorescence intensity. The fluorescence changes indicated that the compound would be able to act as an efficient “off-on-off” switch for pH determination, for monitoring of aggressive environment, e.g., in concrete and industrial pollutants.

Keywords: 3-aminobenzanthrone derivative, ICT (internal charge transfer), pH sensor.

INTRODUCTION

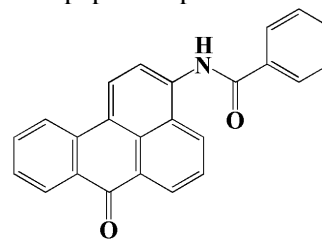
pH is a key parameter for a wide range of applications in the medical field, in environmental and life sciences or for regulation and routine monitoring in industrial processes and in sewage purification plants [1-12]. Fluorescent pH probes usually suffer from optical changes in terms of emission spectra variation and fluorescence intensity. Optical pH sensors based on changes of emission intensity and lifetime have been intensively studied as they can be non-invasive or minimally invasive, disposable, easily miniaturized (down to sub-micrometer), and simple to process (as a coating or solid layer on optical fibers and certain surfaces) for environmental analysis, medical diagnosis, and process control [13-25].

Internal charge transfer (ICT) is one of common principles used for fluorescence molecular switches [26-31]. In the ICT chemosensors the receptor is directly attached to the electron-donating/withdrawing unit that is conjugated to the fluorophore an electron-withdrawing/electron-donating unit. During excitation of the system the fluorophore undergoes donor-acceptor intramolecular charge transfer. The subsequent change in the dipole moment results in a Stokes shift that depends on the microenvironment of the fluorophore. In addition to these shifts, changes in quantum yields and lifetimes are often observed [31-38].

Benzanthrone derivatives attract particular

interest due to their favorable spectral properties - large extinction coefficient, marked Stokes shift, high sensitivity of fluorescence parameters to environmental polarity, etc. [39-43]. Derivatives of benzanthrone are well known as fluorophores emitting fluorescence from yellow-green to orange-red. Bright color and intense fluorescence of benzanthrone gave the impetus to their use as disperse dyes for textiles, daylight fluorescent pigments, dyes for polymers [44-54], lasers, as components in liquid-crystalline systems for electro-optical displays [46, 47, 55-57] or as sensors for biological important metal ions and amines [58-62]. The amidinobenzanthrone derivatives have showed potential as biomedical probes for proteins, lipids, and cells. Such dyes can be also utilized as suitable sensing probes for checking solvent polarity [63-67].

This paper reports on the design and synthesis of novel ICT based amidinobenzanthrone fluorophore (**1**). Also, the photophysical properties of the new compound in presence of protons as cations and hydroxide as anions in solution of DMF/water (1:1) and on cellulose paper are presented.



Formula 1 (**1**).

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EXPERIMENTAL

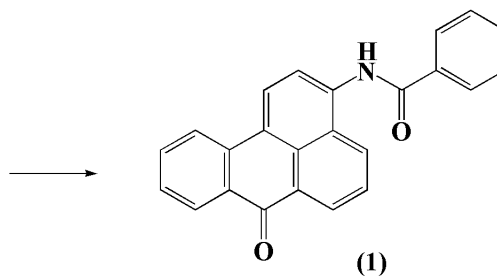
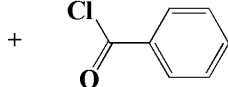
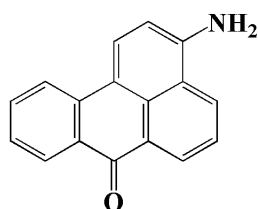
Materials and methods

3-Aminobenzanthrone was prepared [55] by nitration of benzanthrone with fuming nitric acid and subsequent reduction of the nitro group from the 3-nitrobenzanthrone by Na₂S. M.p. = 245–246 °C (cc. [55] 246 °C). Solvents are of p.a or analytical grade (Fluka).

The melting point was recorded on a Büchi 535 apparatus (Switzerland). TLC was made on silica gel plate (Merck, 60 F 254, 20x20 cm, 0.2 mm thickness, ready-to-use).

A pH meter Metrohm 704 coupled with combined pH electrode for the pH measurement was used. The commercial standard buffers for pH 2, 7 and 10 (Aldrich) were used for calibration. The absorption spectra were acquired on Hewlett Packard 8452A spectrophotometer. The fluorescent spectra were recorded on a Scinco FS-2 fluorescence spectrophotometer. The excitation source was a 150 W Xenon lamp. Excitation and emission slits width were 5 nm. Fluorescence measurement was carried out in right angle sample geometry. A 1×1 cm quartz cuvette was used for the spectroscopic analysis of the solutions. Fluorescence measurements on the previously dyed paper were carried using standard buffers.

The fluorescence quantum yields (Φ_F) were measured relatively to Coumarin 6 ($\Phi_F = 0.78$ in ethanol [68] as a standards. All experiments were performed at room temperature (25 °C).



Scheme 1. Synthesis of 3-benzamidobenzanthrone (**1**).

Characteristics of the compound (**1**)

Acylation of the primary amino group with benzoyl chloride was carried out (at reflux during 2 h in dioxane solution). By pouring the reaction mixture into water and filtration the precipitate was obtained. The product was purified by preparative TLC. FT-IR and ¹H NMR spectroscopic studies confirmed the chemical structure of new product.

The photophysical properties of compound (**1**) were investigated in different of polarity solvents at concentration of 1 × 10⁻⁵ mol l⁻¹. Table 1 summarizes the basic spectral characteristics of (**1**) in chloroform, acetone and dimethylformamide (DMF) solutions: the values of absorption (λ_A) and fluorescence (λ_F) maxima, molar extinction

Synthesis of N-(7-oxo-7H-benzo[de]anthracen-3-yl)benzamide or 3-benzamidobenzanthrone (**1**)

3-Aminobenzanthrone [2.45g (0,01 mol)] was dissolved in dioxane (50 mL) and to this solution at 50 °C benzoyl chloride [2.81ml (0,02 mol)] was added drop wise. The temperature was raised to boiling and the mixture was stirred at this temperature for 2 hours. The target compound (**1**) was obtained by pouring into water and filtering. It was purified by preparative thin-layer chromatography (TLC) (n-hexane:acetone = 2/1, v/v) on silica gel.

Yield for crude product 84%, m.p. = 177 °C, R_f = 0.62 (n-hexane:acetone = 2/1, v/v), IR (KBr) cm⁻¹: 3434 (ν-NH), 3055 (ν^{as} ArCH), 1719 (ν-C=O), 1647 (νC=O), 1598 and 1576 (δ-NH), 1303 and 1277 (ν-C-N-), 779 (δArCH);

¹H NMR (CDCl₃, 600 MHz), ppm: 8.80–8.79 (ds, 1H, NH), 8.50–8.46 (m, 4H, ArH), 8.33–8.29 (m, 3H, ArH), 8.10–8.06 (m, 2H, ArH), 7.84–7.81 (t, 1H, ArH), 7.78–7.76 (t, 1H, ArH), 7.67–7.66 (m, 1H, ArH), 7.62–7.60 (m, 1H, ArH), 7.57–7.55 (m, 1H, ArH).

RESULTS AND DISCUSSION

Synthesis of 3-benzamidobenzanthrone (**1**)

The synthetic route used for the preparation of 3-benzamidobenzanthrone (**1**) is outlined in.

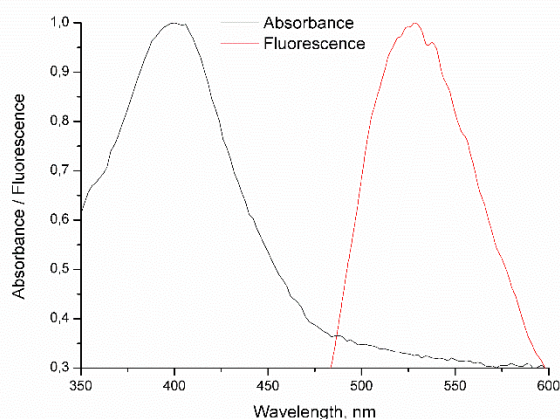
coefficient (ϵ), Stokes shift ($\nu_A - \nu_F$) and quantum yield of fluorescence (Φ_F).

The absorption maximum of (**1**) is shifted hypsochromically if compared to that of 3-aminobenzanthrone (522 nm in dimethylformamide), due to the weaker electron donating ability of the amide group than the amino group.

At room temperature, a weak emission is observed between 480 and 600 nm with λ_F at 515.2 nm (chloroform) till 528.2 nm (dimethylformamide), corresponding to a S₁/S₀ transition. Fig. 1 presents the normalized absorption and fluorescence spectra of (**1**) in dimethylformamide solution as an example.

Table 1. Photophysical characteristics of compound (**1**) in different solvents

Solution	λ_A (nm)	ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)	λ_F (nm)	$\nu_A - \nu_F$ (cm^{-1})	Φ_F
Chloroform	394	10290	515.2	5971	0.29
Acetone	390	11840	517.8	6328	0.21
Dimethylformamide	396	11560	528.2	6320	0.22

**Fig. 1.** Normalized absorption and fluorescence spectra of (**1**) in dimethylformamide solution.

As seen from Fig. 1, the absorption and fluorescence spectra have bands with a single maximum. The fluorescence curve is an approximately equal mirror image of the absorption curve which is indicative of the molecular structure of compound in excited state and prevailing fluorescence emission. The overlap between absorption and fluorescence spectra is low and an aggregation effect for the concentration at about $1 \times 10^{-5} \text{ mol l}^{-1}$ has not been observed.

Influence of pH on absorption and fluorescent properties of probe (1)

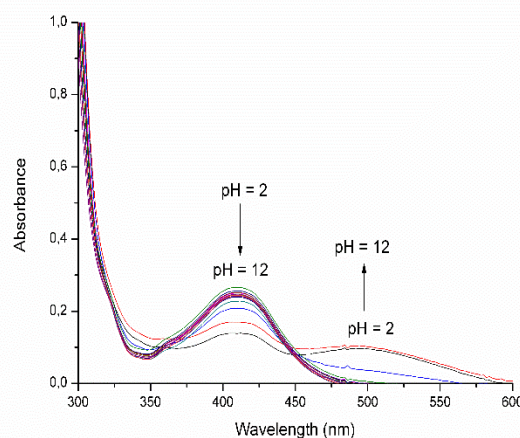
Investigations in solution. The compound under study was designed as fluorescence sensor for determining pH changes over a wider pH scale. This was the reason to investigate the photophysical behaviour of probe (**1**) in water/DMF (1:1, v/v) solution at different pH values.

The basic spectral characteristics of 3-benzamidobenzanthrone depends on the polarization of benzanthrone molecule, due to the electron donor-acceptor interaction occurring between the amino substituent and the carbonyl groups from the chromophoric system. Thus it can be predicted that the interaction of a guest with the donor moiety will change the photophysical properties of the fluorophore.

The amide fragments are widely used functional group in anion recognition. They can recognize anions through hydrogen-bonding and deprotonation interactions [69, 70]. As a result it is expectable that synthesized compound is able to detect anions. When an anion interacts with the benzanthrone

fluorophore amide, the carbonyl electron-accepting ability is reduced due to the deprotonation of the amides which generates a strong electron density near the carbonyl group. In a result the ICT efficiency in the 3-amidobenzanthronic fluorophore increases and red shifting and higher quantum yield are expectable.

With regard to the practical application of (**1**) as a pH sensor, absorption spectra in solution of DMF/water (1:1, v/v) at different pH have been investigated (Fig. 2).

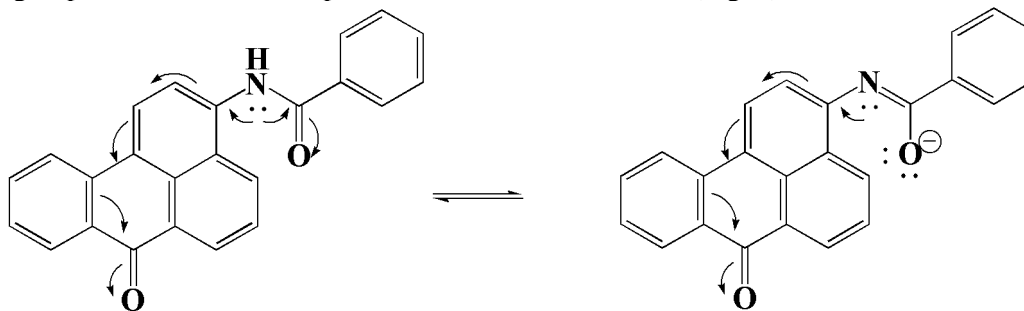
**Fig. 2.** Absorption spectra of compound (**1**) in DMF/water (1:1, v/v) at different pH.

In DMF/water (1:1, v/v) solution compound (**1**) shows longest-wavelength absorption band in range 350-500 nm (in pH range 2-9) and 350-600 nm (in pH range 10-12), which is attributed to the typical for the 3-aminobenzanthrone ICT process. With

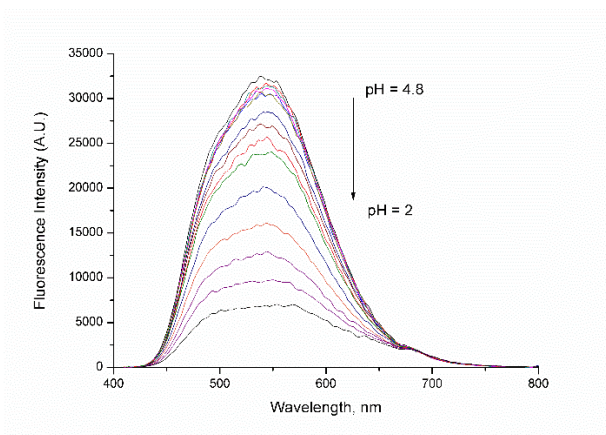
increasing of the alkalinity, the absorption maximum is shifted bathochromically, which corresponded on the deprotonation of the imino group and restores the ICT.

Scheme 2 shows the option for a significant interaction between benzanthrone chromophor and the amide group as receptor via nitrogen atom existing in the molecule of the compound. In this case the unshared electron pair of nitrogen atom interacts with p-electron system of the carbonyl from the amide group, which leads to a partial double

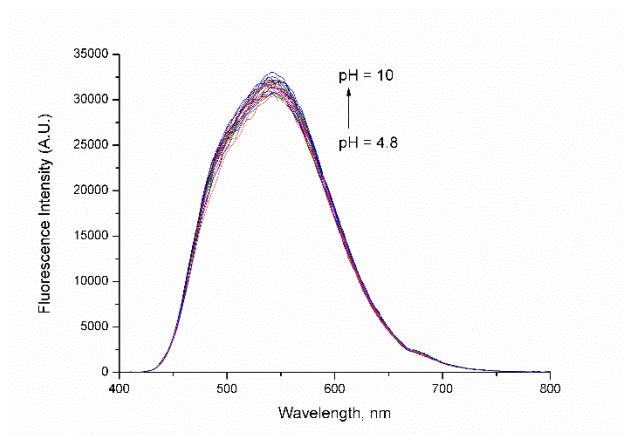
character of the C-N bond. The amide group atoms are located on the same plane and the wide-angle rotation around the C-N amide bond is hindered. In contrast, the unshared electron pair of nitrogen atom interacts with p-electron system of the aromatic chromophore. This leads to an increase in the electron donating properties of the substituent at 3 position of the chromophore molecule and to an increase in the conjugated chromophoric system. As a result, the bathochromic shift in absorption spectra is observed (Fig. 2).



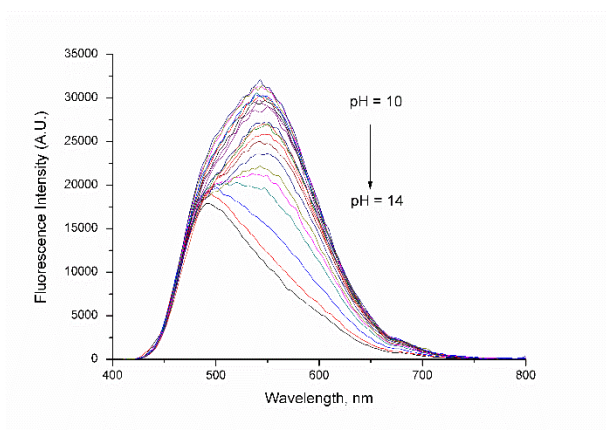
Scheme 2. Schematic presentation of protonated and deprotonated forms of compound **(1)**.



(a)



(b)



(c)

The changes in the fluorescence spectra of compound **(1)** in water/DMF (1:1, v/v) solution at different pH values are depicted in Fig. 3a-c.

Fig. 3. Fluorescence spectra of probe **(1)** in water/DMF (1:1, v/v) solution at different pHs.

The emission spectra of compound under study showed that the compound **(1)** has fluorescence in the range between 430 and 700 nm.

The strongest fluorescence was observed at pH window 4.8-10 with maximum 538.7-541.4 nm (Fig. 3b). At this pH window the molecule is in “on state”. The addition of HCl (pH 4.8-2) to probe (1) converts the imino group in quaternary ammonium cation which strongly decreases the electron donating ability of the nitrogen atom in receptor moiety and decreased the ICT process. At this pH window the compound (1) has fluorescence with maximum at 534.9 nm and the molecule is in “off state” (Fig. 3a). The addition of KOH (pH 4.8-10) to

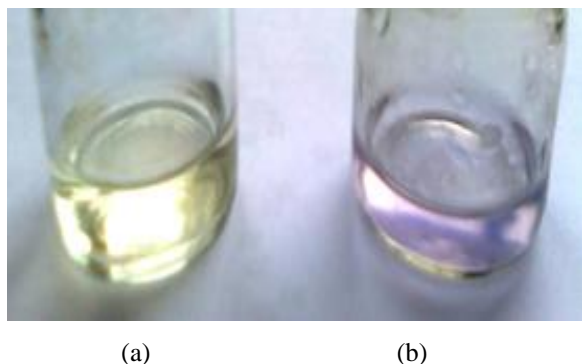


Fig. 4. Change in color of the tested compound in a solution of DMF / water = 1: 1 of neutral (pH 7) (a) in an alkaline (pH 12) (b) medium.

As a whole, a pH titration curve reflecting the “off-on-off” fluorescence response for compound (1) was achieved (Fig. 5). The analysis of the fluorescence changes as a function of pH according to the Eq. (1) gives two pKa values for the compound, for protonated (pKa = 3.55) and deprotonated (pKa = 8) forms respectively.

$$\log [(IF_{\max} - IF) / (IF - IF_{\min})] = \text{pH} - \text{pKa} \quad (1)$$

The calculated quantum yields of fluorescence are: 0.06 (pH 2), 0.17 (pH 8) and 0.04 (pH 12).

Investigations on paper

Because the compound under study was designed as fluorescence sensor for determining pH changes we decided to investigate the photophysical behaviour of compound (1) on paper at different pH values. The obtained paper samples consist of bleached hardwood and softwood pulp in ratio 1:1. The paper weight was 76 g/m². The changes in the fluorescence spectra of compound (1) on paper previously dyed with dye solution with concentration 1.10⁻⁴ g/ml in chloroform at different pH values are depicted in Fig. 6. The emission spectra of compound under study showed that the compound (1) has fluorescence in the range between 430 and 650 nm. The strongest fluorescence was

probe (1) increases the electron donating ability of the nitrogen atom in receptor moiety and increased the ICT process. At this pH window the compound (1) has fluorescence with maximum at 541.4-548.8 nm and the molecule is in “on state” (Fig. 3b). At pH over 10 the fluorescence decreases, because the reduction of carbonyl group occurs probably ($\lambda_{\max}^{\text{fl}} = 492$ nm) (Fig. 3c). There is a visible change in the color of the solution of the tested compound, which is typical for the reduction of the carbonyl group at benzanthrone (Fig. 4).

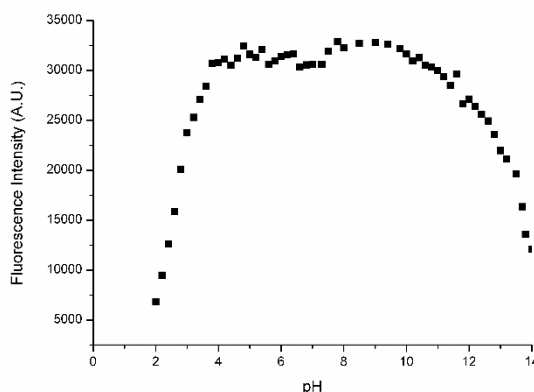


Fig. 5. Fluorescence intensity of compound 1 at 540 nm in water/DMF (1:1, v/v) as a function of pH.

observed at pH 4.5 with maximum 494.2 nm (Fig. 6). At pH 2 the fluorescence was lowest and with maximum at 483.7 nm. The investigation on the paper show similar results as the investigation in solution of water/DMF (1:1, v/v).

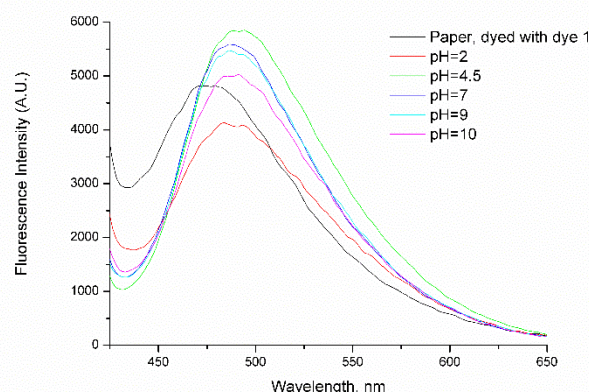


Fig. 6. Fluorescence spectra of probe 1 on paper at different pHs.

CONCLUSIONS

The synthesis and characterization of new 3-benzamidobenzanthrone has been described. The photophysical behavior of new fluorescent pH sensor in DMF/water and on paper as a function of pH was studied. The system is in “on-state” in the

range of pH 4.5-10. The effect was supposed to be related to the deprotonation of the amide receptor in this pH window. The fluorescence changes indicated that the sensors (**1**) would be able to act as an

efficient “off-on-off” switch for pH determination, for monitoring of aggressive environment, e.g., in concrete and industrial pollutants.

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СИНТЕЗА И ФОТО-ФИЗИЧНИ СВОЙСТВА НА НОВ pH-СЕНЗОР С БЕНЗАТРОН НА ОСНОВАТА НА ВЪТРЕШЕН ПРЕНΟΣ НА ЗАРЯДА

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(Резюме)

Синтезиран е нов флуоресцентен сензор, произведен на 3-аминобензантрона, използвайки реакция на нуклеофилно заместване на 3-аминобензантрон с бензоил-хлорид. Сензорът е проектиран като система “флуорофор-рецептор”. Полученото съединение е изолирано и охарактеризирано чрез ТСХ и УВ-Вид спектър, а структурата му - потвърдена с ИЧ и ¹H ЯМР спектри. Поради наличния в молекулата вътрешномолекулен пренос на заряд, синтезираният флуорофор може да се използва като pH проба, оперираща на принципа на “off-on” сензорен механизъм. Изследвана е сензорната активност по отношение на H⁺ и OH⁻ в разтвор ДМФ/вода (1:1) и върху целулоза (хартия), отчитайки промяната във флуоресцентната интензивност. Изследванията показат, че съединението може да бъде използвано като ефективен “off-on-off” превключвател за определяне на pH на среда, за следене на замърсители в околната среда, такива като например индустриални замърсители.